Reversed-phase dispersive liquid-liquid microextraction for elemental analysis in gasoline by inductively coupled plasma optical emission spectrometry

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Abstract

In this work a green and fast sample preparation method based on reversed-phase dispersive liquid-liquid microextraction (RP-DLLME) was developed for the separation and preconcentration of several elements (i.e., Ag, As, Ba, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, S, Se, Sn and V) in gasoline samples before Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES) detection. The extraction procedure was carried out in a reverse mode, since a small volume of aqueous phase (i.e., acidic aqueous solution) is used to extract a relatively high volume of organic phase (i.e., gasoline sample). Unlike conventional DLLME, in the RP-DLLME the analytes were extracted from the organic phase into the aqueous phase. The experimental conditions for the microextraction procedure were: 5 g of amount of sample, HCl 8M as extractant phase, vortex as dispersion system, 115 µL of extractant volume, and 2 min for extraction and 5 min centrifugation time. Under optimized extraction conditions the enrichment factor ranged between 3-53, and limits of detection ranged between 0.02 and 50 µg kg^{-1}. The proposed analytical method was validated and successfully used to analyze three real-world samples (i.e., gasoline). All gasoline samples were spiked at 100 µg kg^{-1} for all analytes, except sulfur (in this case at 1000 µg kg-1), obtaining recovery and RSD values within the range of 88-109% and 2-9%, respectively.

1. Introduction

The presence of trace metals in gasoline, unless they are added purposely, is usually undesirable, as they can be responsible for the poor performance of the gasoline, leading

to deterioration of some engine components [1]. Although some metals are natural constituents of crude oil, others can be found into the gasoline as contaminants (e.g., in the transport and storage container) [2]. Thus, gasoline chemical composition plays an important and essential role, not only for information about fuel quality but also for pollution monitoring [3].

Metallic elements in gasoline are normally present in very low concentration, therefore, it is required the employment of sensitive techniques such as X-Ray Fluorescence (XRF) [4,5], Electrothermal Atomic Absorption Spectrometry (ETAAS) [1,6], Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [7,8], Flame Atomic Absorption Spectrometry (FAAS) [9], and Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES)[10]. ICP OES technique is an excellent option for metal trace determination due to it allows the simultaneous determination of a great variety of elemental analytes due to its high selectivity and sensitivity [11].

Nevertheless, the aforementioned techniques are often not sufficient to achieve the required sensitivity in complex matrices, thus sample pretreatment methods must be used to reach high preconcentration factors. In recent years, Dispersive Liquid-Liquid Microextraction (DLLME) has emerged as an attractive preconcentration method, allowing the extraction and preconcentration of analytes from complex samples [12]. The DLLME technique offers many advantages such as rapid analysis time, simple setup, inexpensive equipment, high extraction efficiency and enrichment factor [13]. The conventional DLLME is carried out in a ternary system composed of an aqueous sample, extractant and dispersant solvents. Thus, the dispersant (e.g., acetonitrile) solvent dispersed the extractant solvent (e.g., chlorinated solvents) into fine droplets increasing the contact area between the sample and the extractant phase, transferring rapidly the analyte from the sample to the extractant phase [14,15]. After extraction and centrifugation steps, the direct analysis of the enriched organic phase into the elemental detection system is discouraged due to incompatibility of the solvent with the technique. For this reason, an additional step of dilution or back extraction is required. When the sample is immiscible with water, aqueous extractant solvent is an excellent option, appearing a new modality of DLLME called Reverse Phase Dispersive Liquid–Liquid Microextraction (RP-DLLME). In this modality, aqueous solvents are employed as extractant solvent [16]. The RP-DLLME provides the ability of introducing the extract (i.e., acidic aqueous solution) directly into the elemental detection system [17].

Recently, Özzeybek et al. reported the determination of cadmium traces in fish and olive oil samples [18], achieving both green and sensitive analytical methods.

The purpose of this work is to present a simple, fast, efficient, and environmentally friendly RP-DLLME procedure, using acidic aqueous solution as a valuable extractant solvent for the simultaneous separation and preconcentration of several elements (i.e., Ag, As, Ba, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, S, Se, Sn and V) in gasoline samples for subsequent measurement by ICP OES.

2. Experimental

2.1. Reagents and real-world samples

Working solutions were prepared from: (i) multi-element standard Conostan S-21 (Conostan, SCP Science, Baie D'Urfé, Canada) containing 500 μg g^{-1} of Ag, Ba, Cd, Cr, Cu, Mn, Mo, Ni, Pb, Sn, and V, and (ii) mono-element stock solution (Conostan) containing 10,000 μg g^{-1} of S, 500 μg g^{-1} of As and Se, and 100 μg g^{-1} of Hg. The solvent used in the calibration standards and as a blank was kerosene (Panreac, Barcelona, Spain; boiling range 190-250 °C). The extractant phase was prepared by an appropriate dilution of an ultra-pure HCl acid (32% w w^{-1}, Merck Pro Analysis, Darmstadt, Germany) in distilled deionized water (18 MΩ.cm resistivity).

The applicability of the analytical method proposed was evaluated using three commercial fuel samples of 95 RON gasoline. The samples were purchased at different petrol stations close to the University of Alicante and were stored in polyethylene terephthalate (PET) containers and kept in the refrigerator until analyzed. Before performing the analysis, the samples were allowed to reach room temperature.

2.2. Instrumentation

All measurements were performed with an inductively coupled plasma optical emission spectrometer (model 720-ES, Agilent Technologies, Melbourne, Australia) working in axially viewed plasma mode. **Table 1** shows the optimum operating conditions and emission lines evaluated in ICP OES. The RF generator power and gas flow rates (i.e., plasma, auxiliary, and nebulizing gas flow rates) were optimized achieving the maximum analyte intensities using a standard solution containing 1 μg g^{-1} of all analytes in kerosene (Panreac), except sulfur in which concentration was 10 μg g^{-1}.

2.3. RP-DLLME optimization

RP-DLLME optimization was performed using a multivariate approach consisting of a Plackett–Burman factorial design in order to identify the significant factors [19]. In these studies, the experiments were randomly performed in order to nullify the effect of extraneous or nuisance factors. After the screening study, only one significant factor was found and univariate optimization was carried out by monitoring the effect of this variable (i.e., extractant volume) on the signal intensity values. On these investigations, a standard solution containing 100 μg kg^{-1} of all analytes was used, except sulfur. In this case a concentration of 2000 μg kg^{-1} was employed.

2.4. RP-DLLME procedure

Under optimized conditions, 5 g of calibration standards or 95 RON gasoline samples were placed in a glass centrifuge tube. Then, 115 μL of aqueous 8 M HCl solution were added and the mixture was shaken for 2 min using vortex agitation. Then, phases were separated by centrifugation for 5 min at 4000 rpm. The upper organic phase was carefully removed with a glass pipette and the remaining acidic aqueous phase (i.e., 100 μL) was retrieved with a syringe for final analysis by ICP OES. **Figure 1** shows a scheme of the overall procedure.

2.5. Data processing

A multivariate optimization strategy was carried out to determine optimum conditions for RP-DLLME. The statistical software NEMRODW® ("New Efficient Methodology for Research using Optimal Design") from LPRAI (Marseille, France) was used to build the experimental design matrix and evaluate the results. In this study, the individual emission intensities were the response functions for optimization.

3. Results and discussion

3.1. RP-DLLME optimization

Numerous factors can affect extraction yield in the RP-DLLME procedure. Therefore, optimization through a multivariate approach was carried out.

3.1.1. Screening study

A Plackett-Burman design was used to construct the matrix of experiments, including six factors in twelve runs. The factors investigated at two levels in this work were:

amount of sample, type of extractant phase, extractant volume, dispersion system, and extraction and centrifugation time. **Table 2** shows the considered experimental factors and levels in the Plackett-Burman design.

Pareto charts of this screening study are shown in **Figure 2**. The relative influence of the corresponding factor, and those bars that exceed reference vertical lines (dashed lines) can be considered significant with 95% probability. In addition, rightward bars indicate a positive effect in the response when increasing from a lower to high level, while leftward bars indicate a negative effect upon the response when passing from a lower to upper level of the corresponding factor. **Figure 2** shows that all the Pareto charts present a similar response for almost all of the factors, varying degrees of significance depending on the analyte. The exceptions are the extraction and centrifugation time which present different effects (i.e., positive or negative) depending on the evaluated analyte. However, the majority of the analytes show a positive effect in the extraction and centrifugation time. Besides, these variables were non-significant. Thus, they were fixed at 2 min (the extraction time) and 5 min (centrifugation time).

Interpretation of the graphic study presented in **Figure 2** leads to conclude that only three factors (i.e., extractant phase type, extractant volume and dispersion system) are statistically significant in the emission lines evaluated. Amount of sample was non-significant with negative effect, and therefore, this factor was fixed at its low level (i.e., 5 g). The type of extractant phase and dispersion system had both positive effects, and they were chosen at their high level (i.e., 8M HCl as extractant phase and vortex as dispersion system). According to a previous publication, this acid plays a significant role in the extraction step, in both organic and inorganic analytes [20,21]. On the other hand, some authors suggest that using the vortex in a mixture of two immiscible liquids directly provides the mechanical energy needed to break up the drop. However, it should be noted there are three different steps that are generated during emulsion formation: deforming, breaking up and rejoining the droplets [22,23]. In accordance with the result of the screening study, the extractant volume was the only factor to be optimized and it was thoroughly studied varying the extractant volume from 115 to 285 μL, with the other factors at the corresponding fixed level.

3.1.2. Optimization study of extractant volume

Figure 3 shows the resulting normalized signal of the average of all emission lines evaluated. The signal of each element was normalized with respect to the maximum signal for each one. In **Figure 3**, the signal intensity decreases by increasing the extractant volume from 115 to 285 µL. It is well known that increasing the extractant volume leads to an increase in metal extraction. In contrast, an excessive extract volume could lead to a dilution effect, thus decreasing the preconcentration factor. It is easy to predict that the optimum extract volume is below 115 µL. However, it was impossible to perform the analysis using a lower volume than 115 µL, since it was the minimum volume required to measure all emission lines analyzed.

Summarizing, optimal RP-DLLME conditions were: 5 g of sample weight, HCl 8M as extractant phase, vortex as dispersion system, 115 µL of extractant volume, and 2 min for extraction and 5 min centrifugation time.

3.2. Validation of the method

The main analytical figures of merit of the proposed method are summarized in **Table 3**. The working range showed good linearity with correlation coefficients (r) from 0.9752 to 0.9997, being the majority of values higher than 0.995. The repeatability of the method was evaluated by analyzing five spiked solutions at 10 and 100 µg kg^{-1}, except sulfur where the spiked concentrations were 500 and 2000 µg kg^{-1}. The obtained RSD % values varied between 3 and 12% (**Table 3**). Enrichment factors (EFs) were calculated as the ratio of the sensitivity obtained with and without RP-DLLME. Arsenic gave the highest extraction performance of the studied analytes, with an EF value of 53, whereas barium showed the lowest extraction performance (i.e., EF=3). LOD values were calculated following the 3 σ_{blank} criteria, being σ_{blank} the standard deviation of 10 blank measurements, in accordance with Eurachem guidelines [24]. Overall emission lines evaluated, barium offered the most sensitive results in the analysis, obtaining a sensitivity of 4000 ± 300 cps kg μg^{-1} and a LOD of 0.02 µg kg^{-1}. Conversely, the highest LOD value was obtained for sulfur (i.e., 50 µg kg^{-1}).

3.3. Analysis of real samples

The original concentrations of the analytes in the three commercial samples analyzed by external calibration were below the LOD, except for sulfur in the three samples and

selenium in samples 1 and 2. Hence, in order to assess the applicability of the proposed analytical method, spiked commercial fuel samples were analyzed. Consequently, the three gasoline samples were spiked at 100 μg kg^{-1} levels of all analytes, except sulfur. In this case, all samples were spiked with 1000 μg kg^{-1} (**Table 4**). According to these results, there were no significant differences between the concentrations added and those found in all gasoline samples, obtaining relative recoveries ranged between 88 and 109%. Therefore, non-significant matrix effects were found with the proposed methodology.

3.4. Comparison with other methods

In order to compare the developed method with previously reported ones, various publications were found in which the same analytes were determined in real fuel samples. The techniques used in the studies consulted differ in either the detection technique or the microextraction technique, or both. In **Table 5** it can be seen that the number of analytes quantified simultaneously is the highest for the developed method. Besides, the time used for the microextraction of the analytes is one of the lowest used thanks to the speed obtained by the RP-DLLME procedure. It should be noted that acidic water solution is a solvent significantly cheaper and greener than other organic solvents and sorbents employed in the bibliography. Even though these publications determinate heavy metals in gasoline samples, to our knowledge, the use of water solution as an extract solvent has not been reported in elemental analysis in gasoline samples. In addition, the analytical method proposed meets with the majority of the 12 principles of Green Analytical Chemistry, especially those related with the reduction of reagents, the use of non-hazardous reagents obtained from renewable sources, the use of miniaturized methods, the safety of the operator, multi-analyte methods, low sample consumption and analytical waste.

4. Conclusions

A RP-DLLME has been investigated for the elemental analysis in commercial fuel samples by ICP OES. The results obtained in this work showed that the RP-DLLME is a successful analytical method for the separation and preconcentration of several analytes from gasoline samples, improving their figures of merits (i.e., a high enhancement factor is obtained) by ICP OES. The application of this microextraction

procedure avoided a laborious and time-consuming digestion procedure that is a mandatory step before the injection of high carbon content samples, resulting in a procedure with very low LOQ. The method was applied to the elemental analysis of three commercial gasoline samples with the additional advantages of using an aqueous extractant solution. The proposed method was carried out using only 115 µL of aqueous 8 M HCl as extractant, reducing drastically the reagent consumption and also the generation of lab residues. In addition, the analytes were extracted to an aqueous phase completely compatible with ICP OES instrumentation, avoiding possible interferences from the organic sample matrix. The results clearly showed that this analytical method is promising and satisfactorily accurate to be used for elemental analysis of gasoline samples by ICP OES.

Acknowledgements

The authors would like to thank the Regional Government of Valencia (Spain) (PROMETEO/2018/087) for the financial support, Agilent Technologies Inc. for the loan of the ICP OES spectrometer, and Ingeniatrics for the OneNeb® provided. Financial support from Universidad Nacional del Sur is gratefully acknowledged. A.S. Lorenzetti E. Vidal and C.E. Domini wish to thank Consejo Nacional de Investigaciones Científicas y Técnicas for the financial support received. The authors extend their appreciation to Ministry of Science, Innovation and Universities for granting the Spanish Network of Excellence in Sample Preparation (RED2018-102522-T). This article is based upon work from the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society.

Table 1. Operating conditions for ICP OES.

Parameters	Value
Nebulizer type	OneNeb®
Spray chamber	Cyclonic
RF generator power	1200(W)
Plasma gas flow rate (L min^{-1})	15
Auxiliary gas flow rate (L min^{-1})	1.5
Nebulizing gas flow rate (L min^{-1})	0.75
Sample liquid flow (µL min^{-1})	100
Replicates	3
Viewing mode	Axial
Emission lines (nm)	Ag (328.068), As (193.696), Ba (455.403), Cd (214.439), Cr (267.716), Cu (324.754), Hg (253.652), Mn (257.610), Mo (202.032), Ni (216.555), Pb (220.353), S (181.972), Se (196.026), Sn (283.998) and V (311.837).

Table 2. Experimental factors and levels of the Plackett-Burman design.

Experimental factor	**Low level (-1)**	**High level (+1)**
Amount of sample (g)	5	7
Type of extractant phase	HNO_3 (8M)	HCl (8M)
Extractant volume (µL)	150	250
Dispersion system	Ultrasound	Vortex
Extraction time (min)	1	2
Centrifugation time (min)	3	5

Table 3. Analytical figures of merit of the proposed method (RP-DLLME/ICP OES).

Analyte	Working range (μg kg^{-1})	r[a]	Sensitivity (cps kg μg^{-1})[b]	RSD (%)[c]		LOD (μg kg^{-1})	LOQ (μg kg^{-1})	EF[d]
				10 (μg kg^{-1})	100 (μg kg^{-1})			
Ag	10-150	0.9967 (4)	232±6	11	8	1.5	5	9
As	50-200	0.9752 (4)	10.5±0.2	-	7	6	20	53
Ba	0.10-150	0.9985 (6)	4000±300	4	7	0.02	0.05	3
Cd	1.0-150	0.9987 (5)	179±7	9	8	0.15	0.5	14
Cr	1.0-150	0.9988 (5)	176±5	11	7	0.3	1.0	7
Cu	1.0-150	0.9955 (5)	275±13	13	6	0.12	0.4	9
Hg	10-150	0.9997 (4)	89.9±1.9	9	8	0.9	3	24
Mn	0.10-200	0.9977 (6)	1340±70	6	10	0.03	0.10	13
Mo	10-150	0.9959 (4)	70±3	12	11	1.2	4	20
Ni	10-150	0.9945 (4)	55±4	11	8	1.2	4	17
Pb	10-150	0.9964 (4)	18.78±0.05	11	5	3	9	15
S	500-2000	0.9832 (4)	3.22±0.09	12*	3*	50	150	5
Se	50-200	0.9975 (4)	2.2±0.5	-	10	12	40	5
Sn	10-150	0.9996 (4)	20.4±0.8	12	7	3	10	8
V	1.0-150	0.9981 (5)	640±70	10	11	0.09	0.3	25

[a] Correlation coefficient (r): number of calibration standards in parentheses.
[b] Slope ± standard deviation.
[c] Relative standard deviation (RSD): mean value for 5 replicate analyses of 10 and 100 μg kg^{-1} spiked solution. * In case of sulfur the spiked concentrations were 500 and 2000 μg kg^{-1}.
[d] Enrichment factor (EF): calculated as the ratio of the sensitivity obtained with and without RP-DLLME.

Table 4. Analytical results obtained in the analysis of three spiked gasoline samples. The concentration and recovery values are expressed as the mean ± standard deviation of the three replicates.

Analyte	Spike ($\mu g\ kg^{-1}$)	Sample 1		Sample 2		Sample 3	
		Concentration ($\mu g\ kg^{-1}$)	R (%)	Concentration ($\mu g\ kg^{-1}$)	R (%)	Concentration ($\mu g\ kg^{-1}$)	R (%)
Ag	-	<LOQ	-	<LOQ	-	<LOQ	-
	100	101±5	101±5	91±6	91±6	105±5	105±5
As	-	<LOQ	-	<LOQ	-	<LOQ	-
	100	93±4	93±4	95±5	95±5	93±4	93±4
Ba	-	<LOQ	-	<LOQ	-	<LOQ	-
	100	102±3	102±3	91±4	91±4	105±4	105±4
Cd	-	<LOQ	-	<LOQ	-	<LOQ	-
	100	92±6	92±6	103±3	103±3	106±7	106±7
Cr	-	<LOQ	-	<LOQ	-	<LOQ	-
	100	90±4	90±4	94±4	94±4	93±5	93±5
Cu	-	<LOQ	-	<LOQ	-	<LOQ	-
	100	106±5	106±5	105±3	105±3	108±3	108±3
Hg	-	<LOQ	-	<LOQ	-	<LOQ	-
	100	90±7	90±7	92±4	92±4	107±4	107±4
Mn	-	<LOQ	-	<LOQ	-	<LOQ	-
	100	102±5	102±5	93±4	93±4	105±4	105±4
Mo	-	<LOQ	-	<LOQ	-	<LOQ	-
	100	98±7	98±7	94±3	94±3	96±5	96±5
Ni	-	<LOQ	-	<LOQ	-	<LOQ	-
	100	99±6	99±6	93±4	93±4	91±7	91±7
Pb	-	<LOQ	-	<LOQ	-	<LOQ	-
	100	88±6	88±6	101±3	101±3	99±5	99±5
S	-	1978±81	-	1674±113	-	1354±138	-
	1000	2936±147	96±5	2604±87	93±6	2394±79	104±7
Se	-	97±6	-	51±4	-	<LOQ	-
	100	199±12	102±6	160±8	109±4	103±8	103±8
Sn	-	<LOQ	-	<LOQ	-	<LOQ	-
	100	98±2	98±2	107±9	107±9	106±4	106±4
V	-	<LOQ	-	<LOQ	-	<LOQ	-
	100	94±4	94±4	98±5	98±5	107±5	107±5

Table 5. Comparison between different methods for elemental analysis in fuel samples.[a]

Detection Technique	Sample preparation	Sample	Analyte	Extraction time (min)	Enrichment Factor	LOQ ($\mu g\ L^{-1}$)	Reference
EDXRF	MSPME	Ethanol Fuel	Cu, Cd, Pb, Cr, V, Mn	11	NI	36 (Cu), 39 (Cd), 48 (Pb), 36 (Cr), 27 (V), 33 (Mn)	[4]
EDXRF	RP-VALLME	Diesel oil	Cu, Mn, Ni, Pb	<1	34 (Cu), 62 (Mn), 59 (Ni), 64 (Pb)	47 (Cu), 26 (Mn), 34 (Ni), 23 (Pb)	[5]
ETAAS	MIL DLLME	Gasoline and diesel	Cd	2	220	0.28*	[1]
ETAAS	Emulsion breaking and DLLME	Biodiesel and oil	Cu, Pb	30	18 (Cu), 2.5 (Pb)	0.76 (Cu), 0.81 (Pb)	[6]
ICP-MS	Emulsion breaking	Gasoline	Cd, Mn, Pb, Sb	<1	NI	0.1 (Cd), 2 (Mn), 0.2 (Pb), 0.07 (Sb)	[7]
ICP-MS	HF-SPME	Gasoline and diesel	Cd, Cu, Fe, Pb, Zn	40	NI	0.4 (Cd), 0.3 (Cu), 0.5 (Fe), 0.9 (Pb), 0.3 (Zn)	[8]
FAAS	Emulsion breaking	Gasoline	Cu, Fe, Pb	10	2.4 (Cu), 2.5 (Fe), 2.0 (Pb)	11 (Cu), 77 (Fe), 48 (Pb)	[9]
ICP OES	HF-LPME	Gasoline and diesel	Ag, Al, As, Mn, Ti	55	150 (Ag), 291 (Al), 112 (As), 405 (Mn), 367 (Ti)	0.27 (Ag), 0.18 (Al), 0.29 (As), 0.15 (Mn), 0.17 (Ti)	[10]
ICP OES	RP-DLLME	Gasoline	Ag, As, Ba, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, S, Se, Sn and V.	2	9 (Ag), 53 (As), 3 (Ba), 14 (Cd), 7 (Cr), 9 (Cu), 24 (Hg), 13 (Mn), 20 (Mo), 17 (Ni), 15 (Pb), 5 (S), 5 (Se), 8 (Sn), 25 (V)	5 (Ag), 20 (As), 0.05 (Ba), 0.5 (Cd), 1.0 (Cr), 0.4 (Cu), 3 (Hg), 0.10 (Mn), 4 (Mo), 4 (Ni), 9 (Pb), 150 (S), 40 (Se), 10 (Sn), 0.3 (V)*	This work

[a] ET, extraction time; NI, not indicated; MIL DLLME, magnetic ionic liquid dispersive liquid-liquid microextraction; EDXRF, energy dispersive X-ray fluorescence spectrometry; MSPME, magnetic solid phase microextraction; HF-SPME, hollow fiber solid phase microextraction; HF-LPME, hollow fiber-liquid phase microextraction; RP-VALLME, reversed-phase vortex-assisted liquid-liquid microextraction.

*LOQ values expressed in $\mu g\ kg^{-1}$.

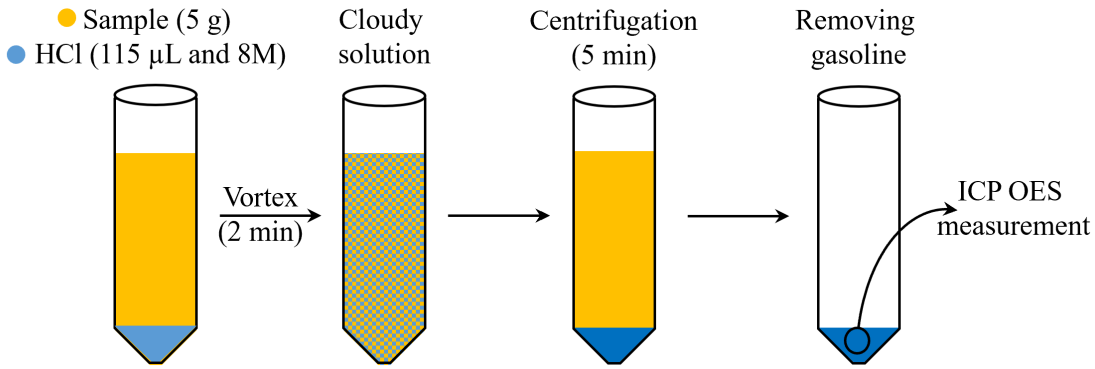

Figure 1. Scheme of the analytical procedure.

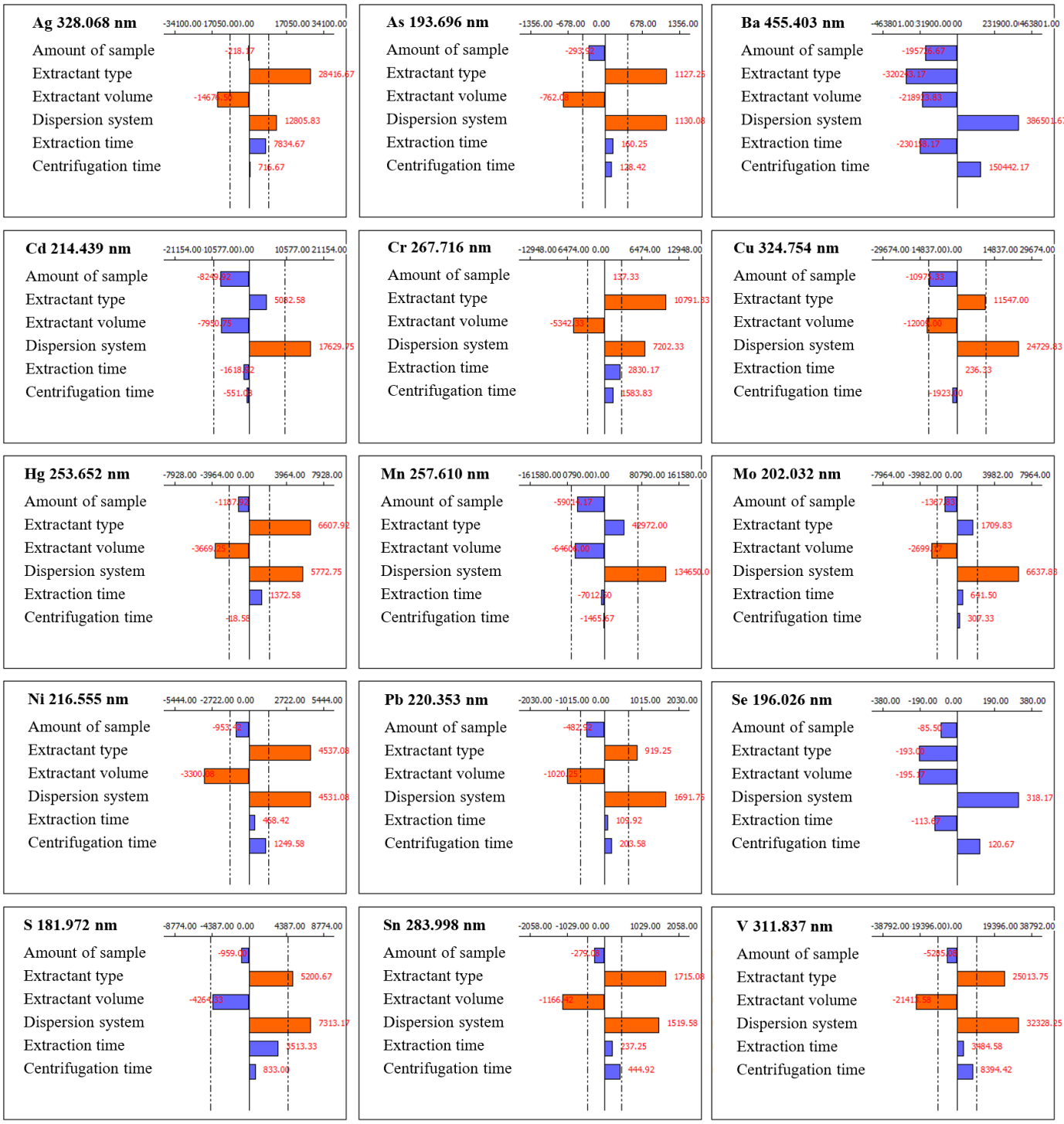

Figure 2. Pareto charts obtained in the screening study of the experimental factors affecting the RP-DLLME for all the evaluated emission lines.

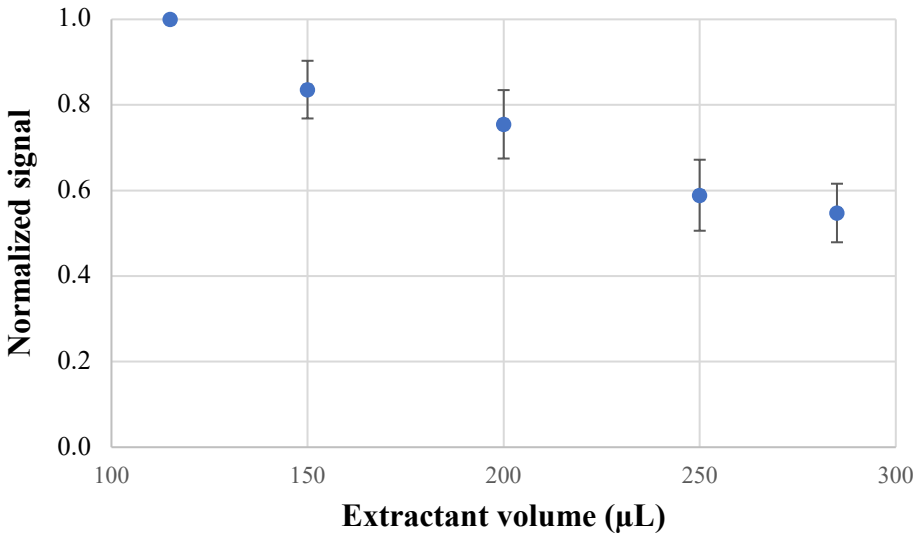

Figure 3. Effect of the extractant volume in RP-DLLME. Error bars represent the standard deviation of all emission lines evaluated. The experimental conditions for the microextraction procedure were: 5 g of amount of sample, HCl 8M as extractant phase, vortex as dispersion system, and 2 min for extraction and 5 min centrifugation time.

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